

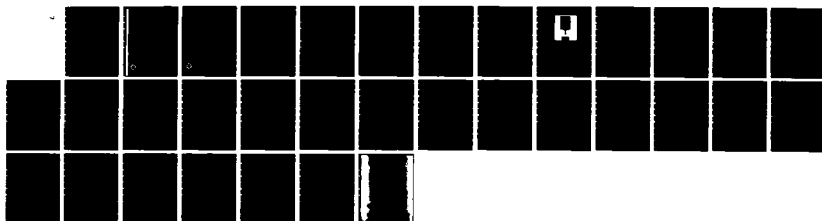
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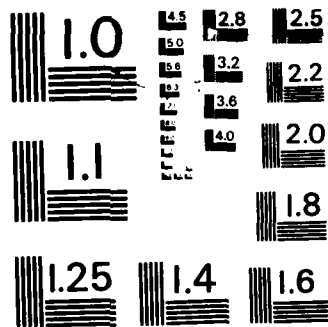
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SPECTROSCOPY (CEMS) OF IRON-DOPED INP(U) OLD DOMINION
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FINAL TECHNICAL REPORT

FEASIBILITY STUDIES OF CONVERSION ELECTRON
MOSSBAUER SPECTROSCOPY (CEMS) OF IRON-DOPED InP

By

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May 1984

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FEASIBILITY STUDIES OF CONVERSION ELECTRON
MÖSSBAUER SPECTROSCOPY (CEMS) OF
IRON-DOPED InP

By

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Norfolk, VA 23508

ABSTRACT

An electron detector for conversion electron Mössbauer spectroscopy (CEMS) has been designed and built. Tests have been performed to study the effects on the detector resolution with respect to high voltage, gas flow rate, and counting rate. These parameters have been optimized to detect the 7.3keV conversion electrons emitted following resonant absorption of the 14.4keV source gamma rays associated with the Mössbauer effect using ^{57}Fe . CEMS spectra have been obtained using standard ^{57}Fe enriched and natural iron samples. CEMS spectra have also been obtained for InP:Fe samples supplied by the Naval Research Laboratory. So far we have only been successful in observing the iron in the precipitates in these samples. Our tentative conclusions are that the precipitate regions contain a FeP_2 component and perhaps regions of pure iron. We intend to study the precipitates further. Since our preliminary work has been completed, we now plan to make extensive tests to determine whether or not the CEMS technique can detect the substitutional iron in InP:Fe samples.

I. INTRODUCTION

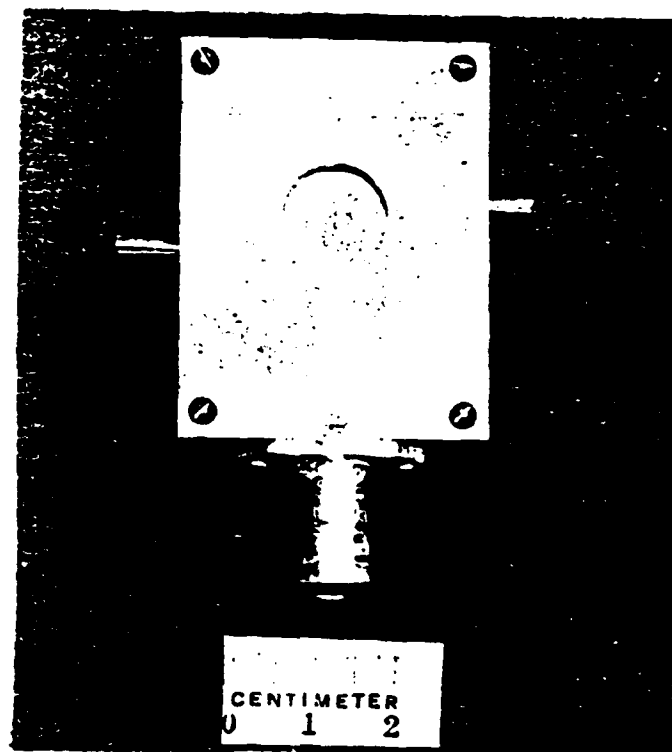
Conversion electron Mössbauer spectroscopy^{1,2} appears to have great potential for utilization in the study of solid state physics problems. This is true because of its surface sensitivity and potentially large signal-to-noise (S/N) capability. In our initial studies, in order to optimize the S/N, we have investigated the properties of one type of electron detector as reported below in Section II. We have also been able to obtain CEMS spectra for absorber samples of; enriched (30%) Fe in rhodium foil, non-enriched stainless steel foil, enriched (95%) iron foil, and samples of ⁵⁷Fe doped InP. In the latter case we have, so far, only observed the iron phosphide precipitates in the samples of interest. We are in the process of making a careful study of these precipitates due to the fact that there has been some controversy about their nature, i.e., FeP, FeP₂, etc. However, our ultimate objective is to determine the contributions of the various iron ionic states that are substitutionally present in the useful semi-insulating InP:Fe samples.

II. EXPERIMENTAL OPTIMIZATION

In Fig. 1, we show a design for a conversion electron detector developed by the National Bureau of Standards.³ Our first detector is similar to that shown except the dimensions are slightly altered and the high voltage wire is supported in a different fashion. The entrance window is covered with a 3mm thick lucite plate to absorb 6.4keV Fe K x-rays from the ⁵⁷Co Mössbauer source. This lucite plate is placed just behind a 0.0025" aluminum foil filter which also helps to attenuate non-Mössbauer radiation thus greatly increasing the efficiency of the detector. The material forming the detector cavity is composed of a low atomic number material, in this

Figure 1.

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Photograph of detector for conversion electrons.

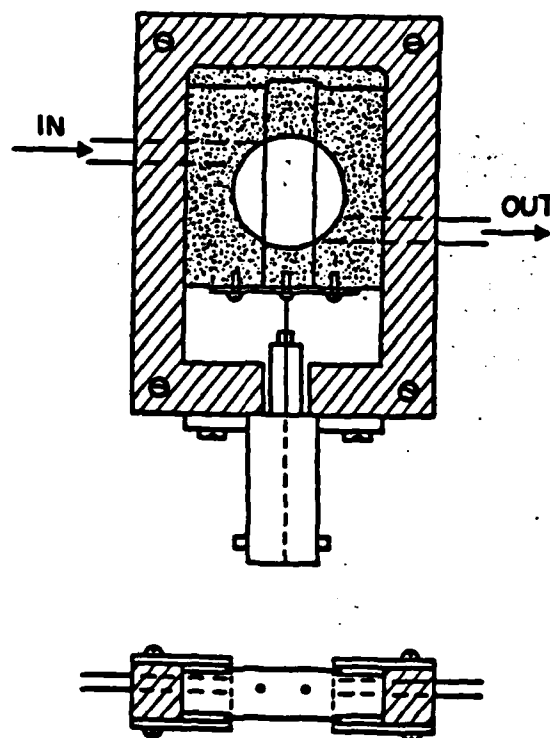


Diagram of detector for conversion electrons.

case lucite, in order to suppress the number of undesired electrons created by incident photons striking the walls of the cavity material. The anode consists of a length of 0.025mm diameter tungsten wire which is inserted into two holes drilled through the lucite detector cavity. The top and bottom aluminum plates are secured to the main chassis of the detector with screws. Rubber gaskets ensure a good seal for these plates. The basic experimental arrangement is such that the ^{57}Co in rhodium source is moved at varying velocities with respect to the detector which contains the sample under study. The resulting doppler-shifted resonant gamma rays emitted by the source enter the detector through the entrance window, shown as a circle in the bottom of Fig. 1 and seen in the accompanying photograph. The absorber (i.e. sample) is placed over the exit window of the same shape and size. The gamma rays strike the sample and nuclear resonant absorption can occur at the ^{57}Fe sites. When such an excited nucleus decays it is most likely to emit a conversion electron from the K shell of the iron ion. It is these electrons which must be counted by the detector. In order to detect the conversion electrons and not the incoming 14.4keV gamma rays, or subsequently emitted x-rays, the gas in the detector was chosen to be helium with 10% methane. The methane provides the positive pulse quenching action. A low pressure gas regulator (Matheson model 3702, 0-5 psig) is used to control the flow rates to $\pm 0.1\text{cc/min}$. Flow rates between zero and 20cc/min. are measured with a mass flow transducer (Hastings model LF20) inserted in the gas line to the detector.

We determined very quickly that it is extremely important that the gas does not leak from the sensitive volume, i.e., the cylindrical space between the two circular windows inside the detector. The resolution of the detector was also improved by ensuring that the exposed surfaces in the sensitive

volume were grounded. This was accomplished by spraying the cylindrical inner wall with aluminum paint and by placing aluminum foils in front of and behind the sample.

In order to test the properties of the electron detector a series of tests were performed. The tests were performed using our "matched" 30% enriched iron in rhodium absorber. The point here is that this absorber is in resonance with our source when the source is at rest, i.e., the relative velocity is zero. When the drive is turned on and the source is moving through a large velocity range the source and absorber are only in resonance for that fraction of the time when the source is instantaneously at rest. In this way one can obtain an electron energy distribution both "on" and "off" resonance.

For the initial tests of the detector, presented below, the source was at rest, and the system was in resonance. Thus, when resonance 7.3keV conversion electrons are produced in the absorber some will leave the absorber and move into the sensitive volume of the detector. Generally, of course, unwanted "noise" electrons will also be present. The output pulses from the detector are fed into a pre-amplifier, an amplifier and, finally, into a multichannel analyzer. The multichannel analyzer is set to run in the pulse height analysis mode. In this way, the number of electrons detected as a function of their energy could be recorded.

In Figs. 2, 3, and 4, we show some of our results when the high voltage is changed. For these runs the source to absorber distance was kept fixed at 5/8" and the gas flow rate was kept at 3cc/min. As will be shown later, the conversion electron peak is associated with the rounded step on the right side of the curve in Fig. 2. As the d.c. voltage of the wire in the detector is increased, the rounded step moves out in energy and broadens.

Figure 2.

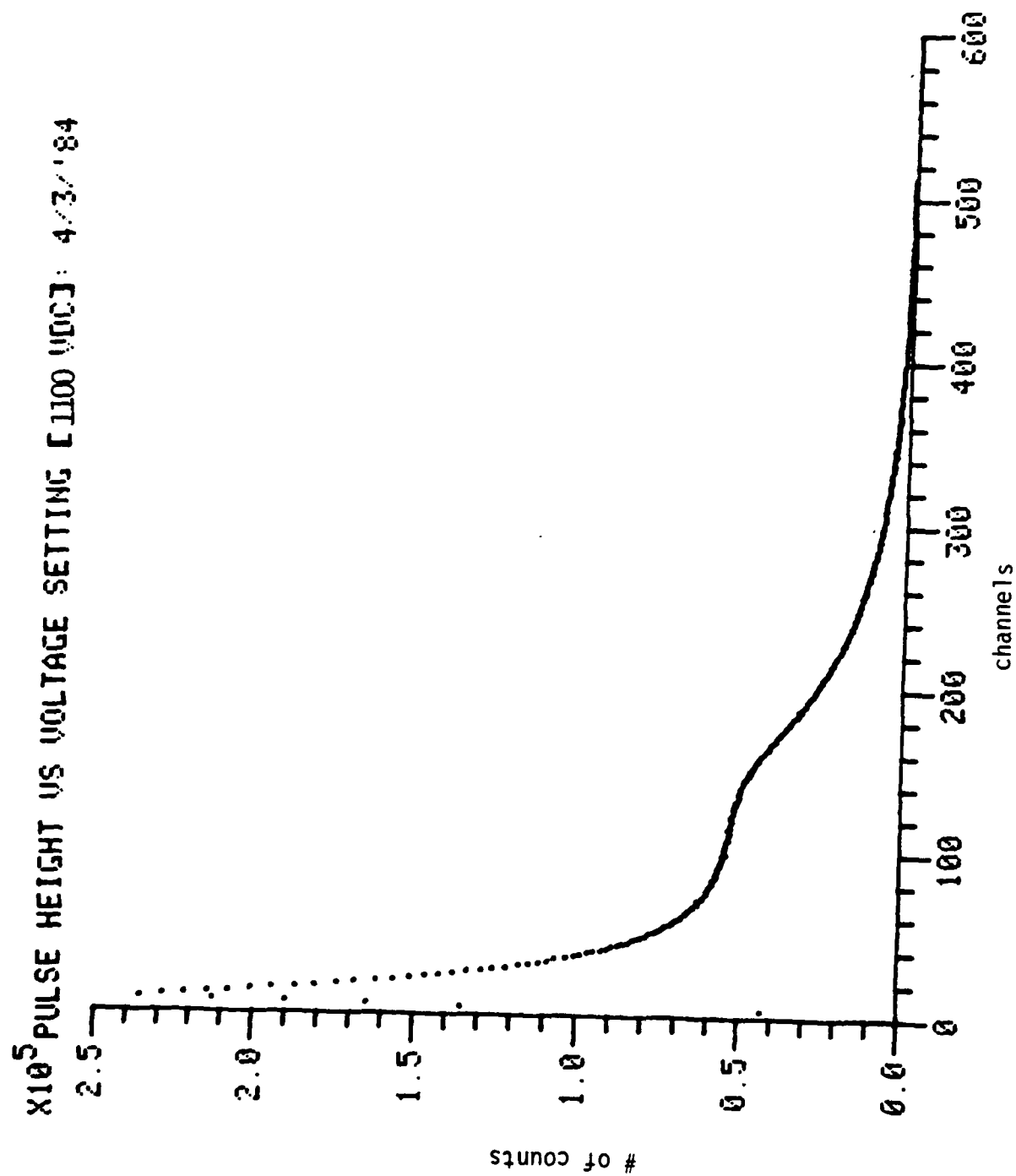


Figure 3.
PULSE HEIGHT VS. VOLTAGE SETTING L1150 VDC J 4/3/'84

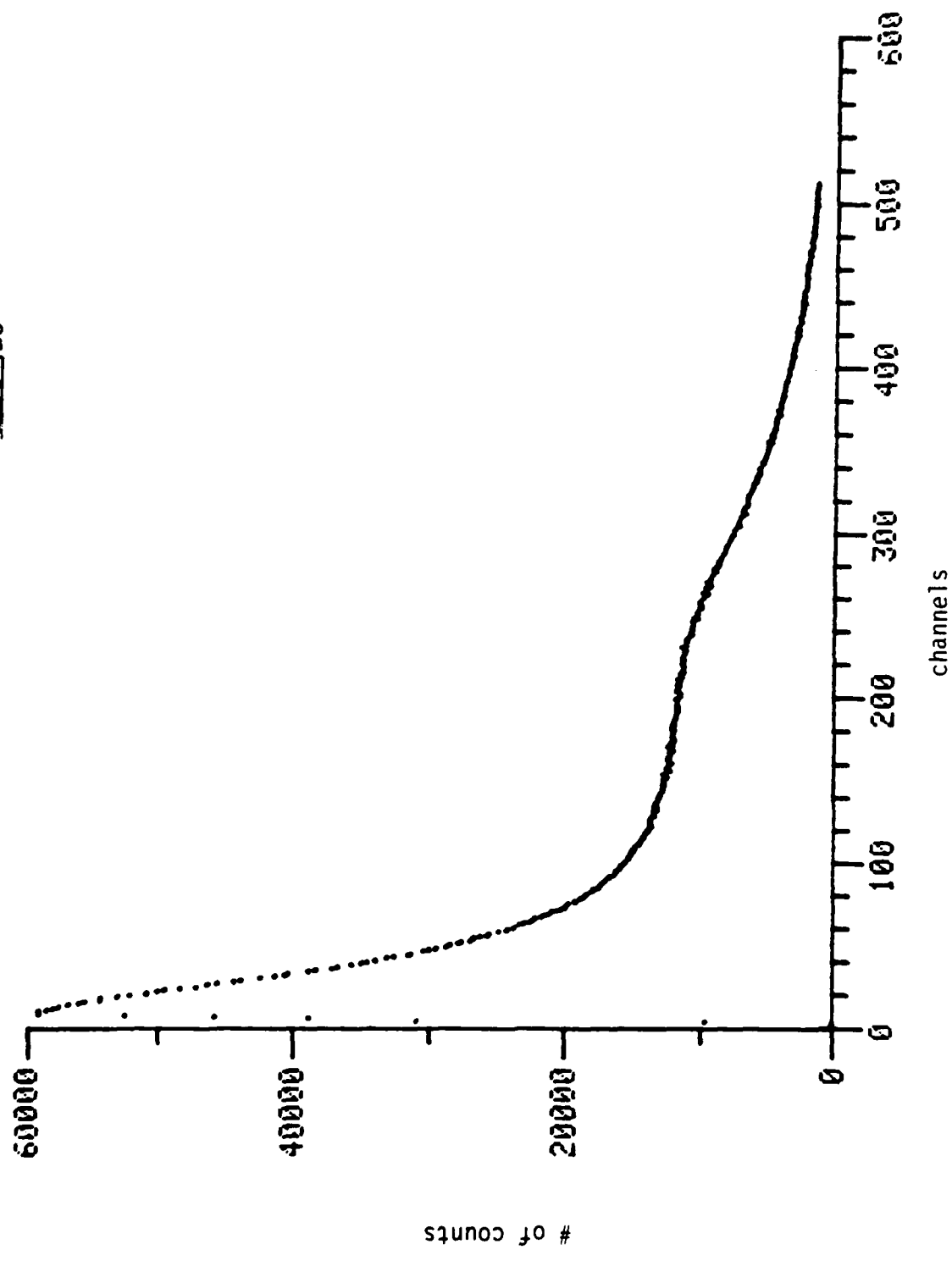
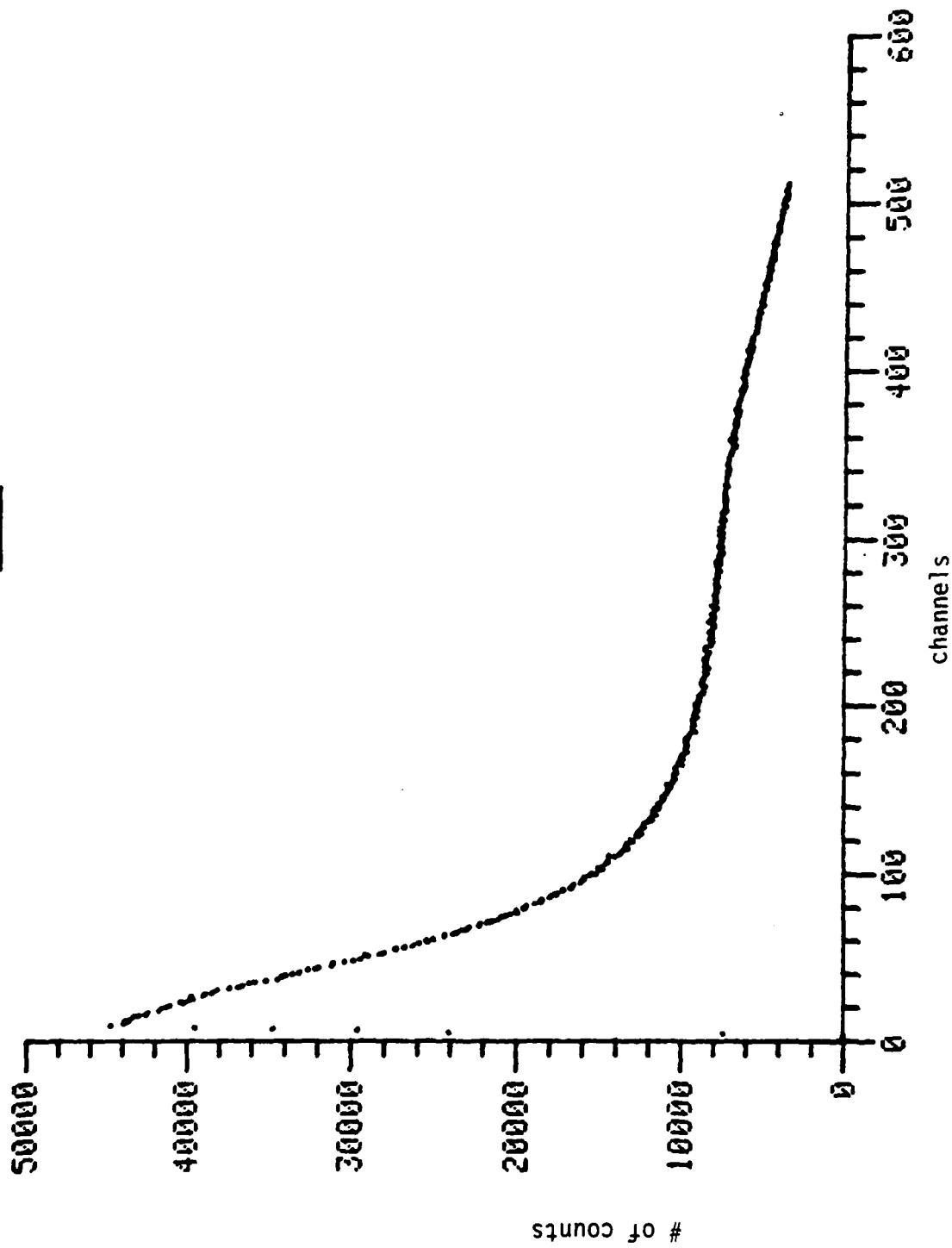


Figure 4.

PULSE US. VOLTAGE SETTING [1200 VDC] 4/3/'84



This is just what one would expect.

Figs. 5 and 6 show some of our results of the detector's responses to count rate. For these data the high voltage was kept fixed at 1180 VDC and the gas flow rate was kept fixed at 3cc/min. However, in Fig. 5 the source to absorber distance was 0.5" while in Fig. 6 this distance was 3.2". The location of 7.3keV conversion electron peak for these two cases was around channel 300. The closer distance did not seem to adversely effect the resolution of the detector.

In Figs. 7, 8, 9, and 10, data are presented which show the detected electron energy distribution as a function of gas flow rate. For these data the voltage was kept constant at 1100 VDC and the source to absorber distance was 5/8". The flow rates used in Figs. 7-10 were 2, 3, 4, and 5cc/min, respectively. As the flow rate increases the gain of the detector increases. This is seen by noting the location of the 7.3keV conversion electron "shoulder" on the pulse height spectra. At 5cc/min, this shoulder is located at about channel 300.

It is useful to determine the pulse height distribution associated with just the 7.3keV conversion electrons. This can be done by taking a pulse height spectrum "on" resonance and subtracting the pulse height spectrum "off" resonance. For our "matched" set of source and absorber, this can be done by running a pulse height spectrum with the drive off, i.e., $v = 0$, and subtracting the result when the source drive is turned on using a large velocity range setting. The result of such an experiment is shown in Fig. 11. (The "on" resonance pulse height spectrum corresponding to this case is shown in Fig. 9.) Notice that the pulse height spectrum of the 7.3keV conversion electrons themselves is rather broad and, hence, there are "good" counts over almost the whole energy range.

Figure 5.

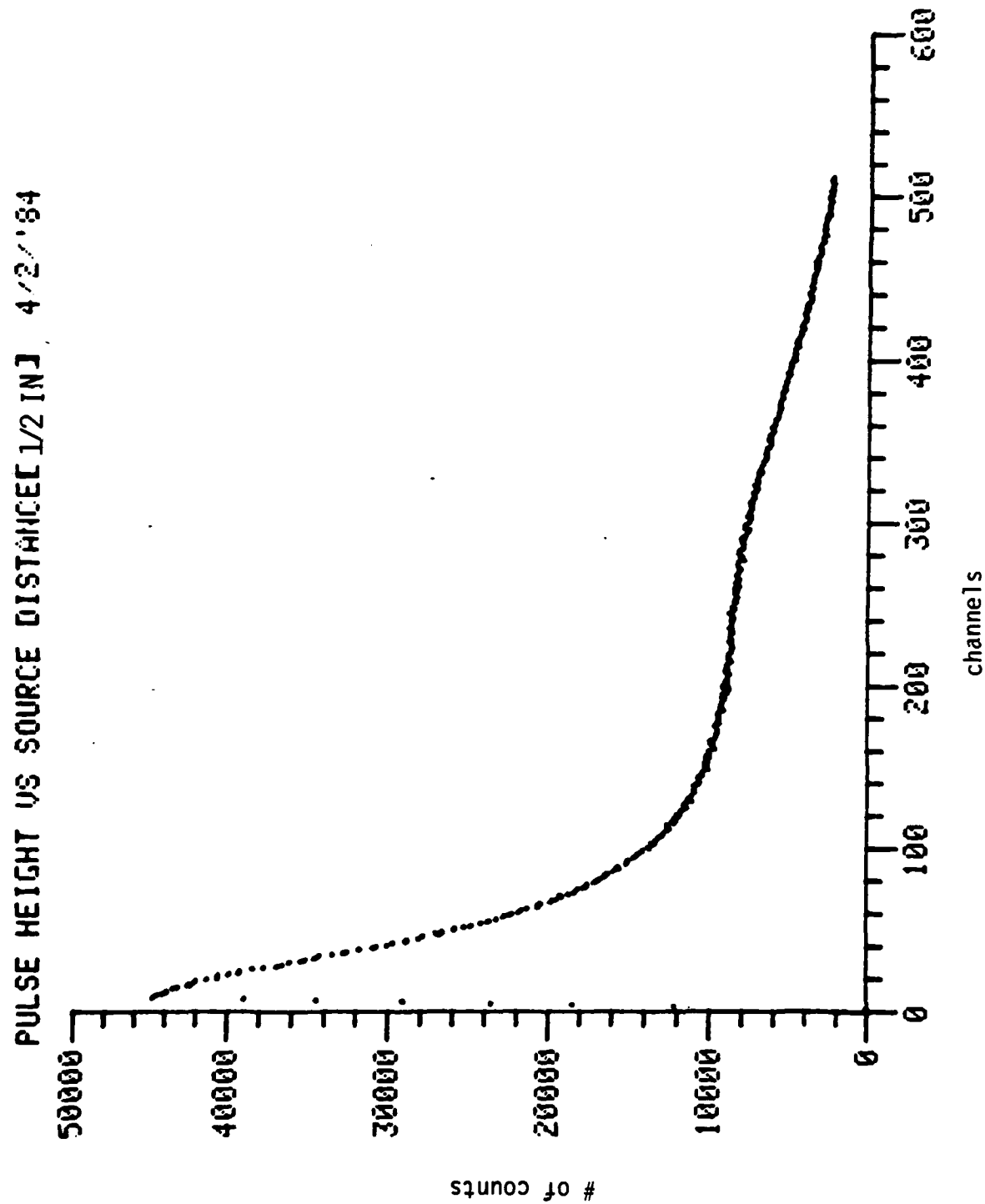
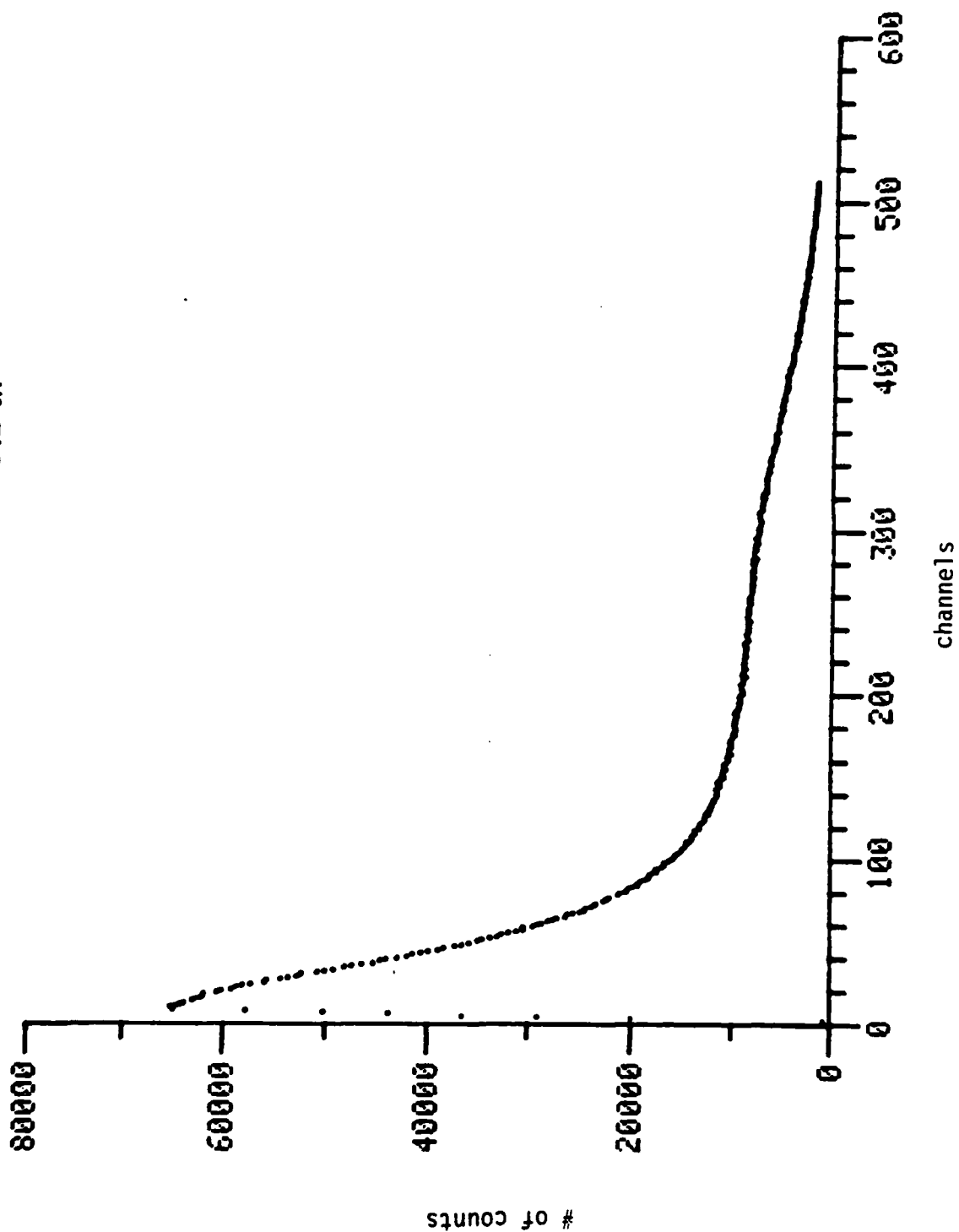


Figure 6.

PULSE HEIGHT VS. SOURCE DISTANCE [3.2 IN] 4/2/'84



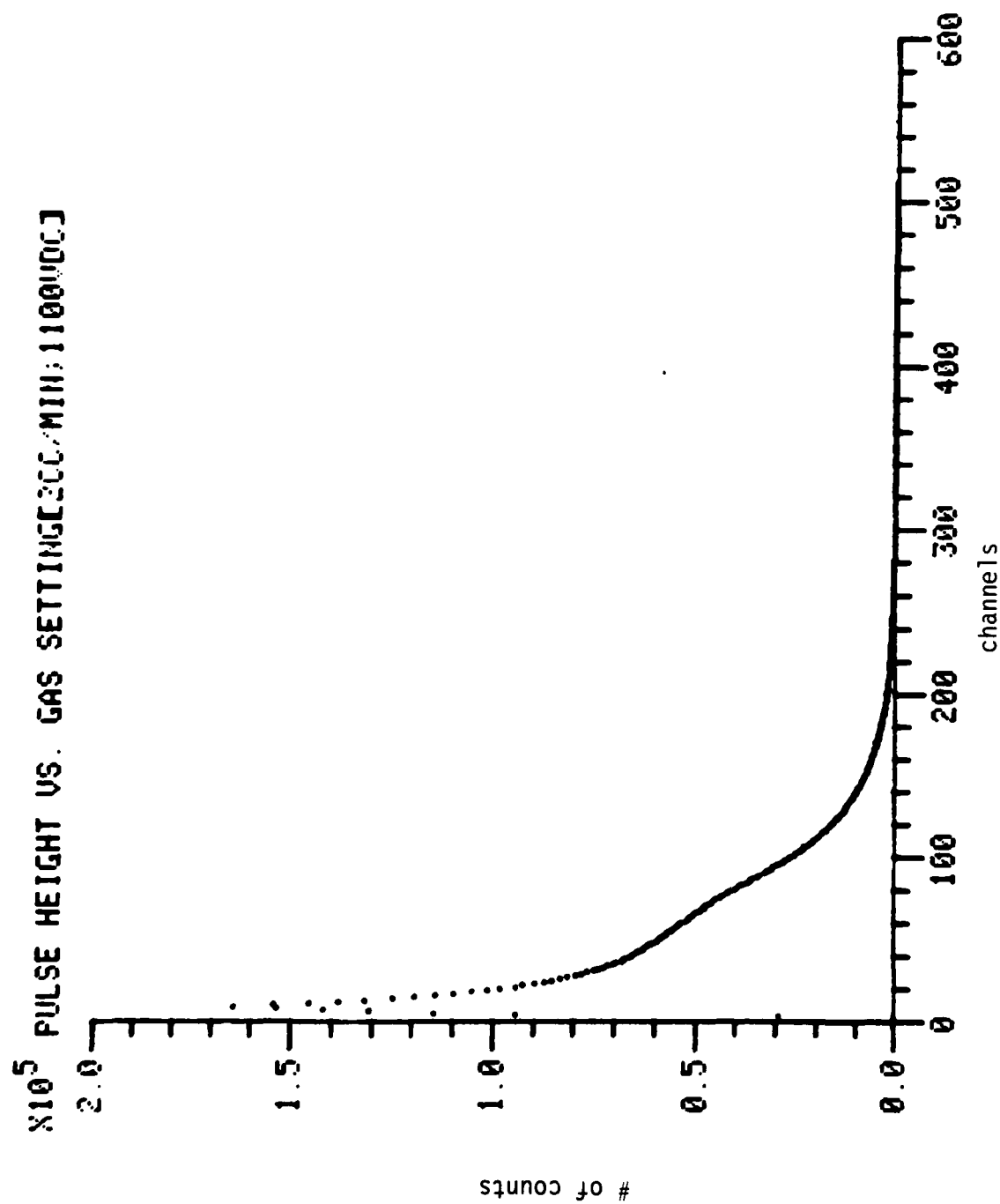


Figure 7.

Figure 8.

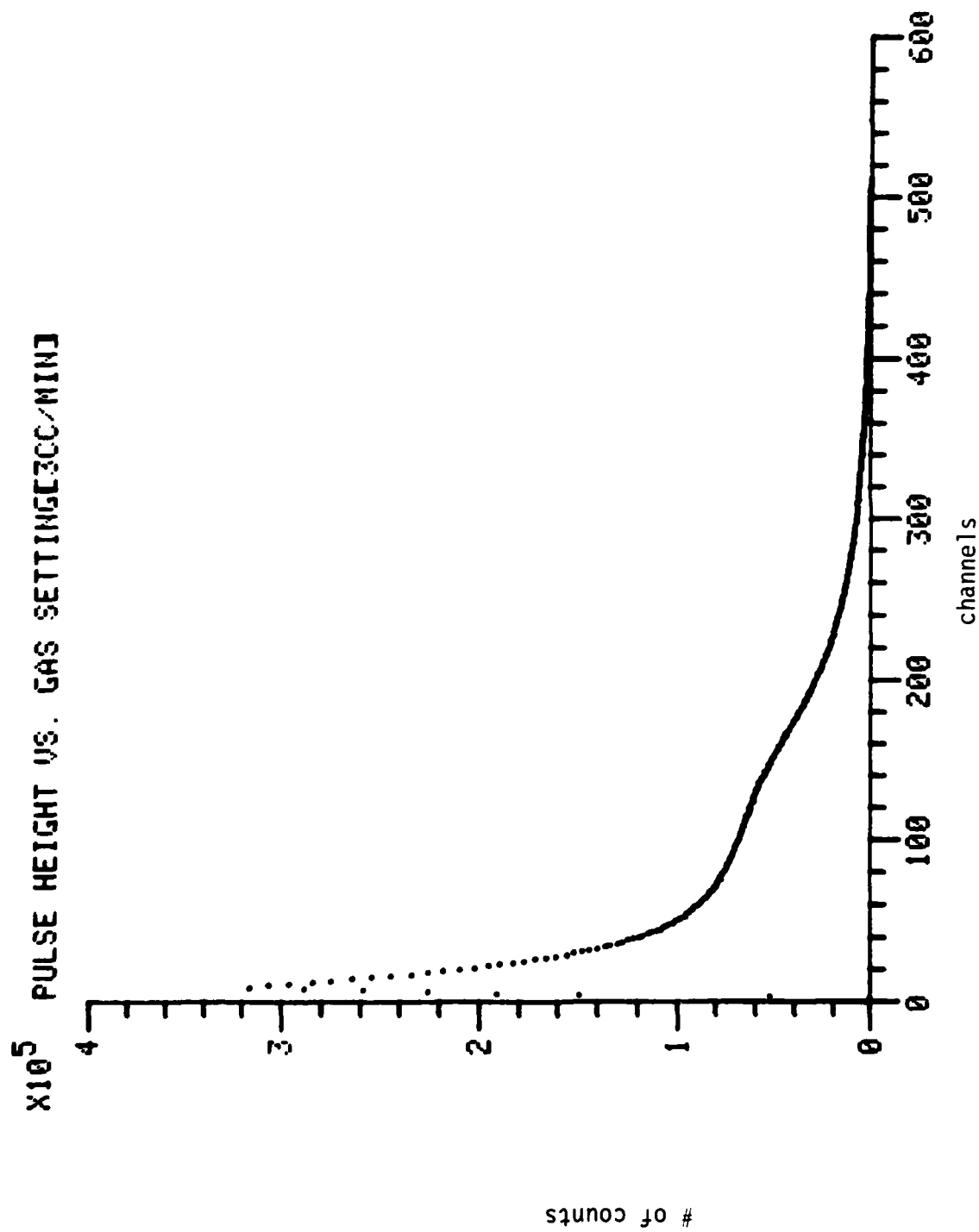
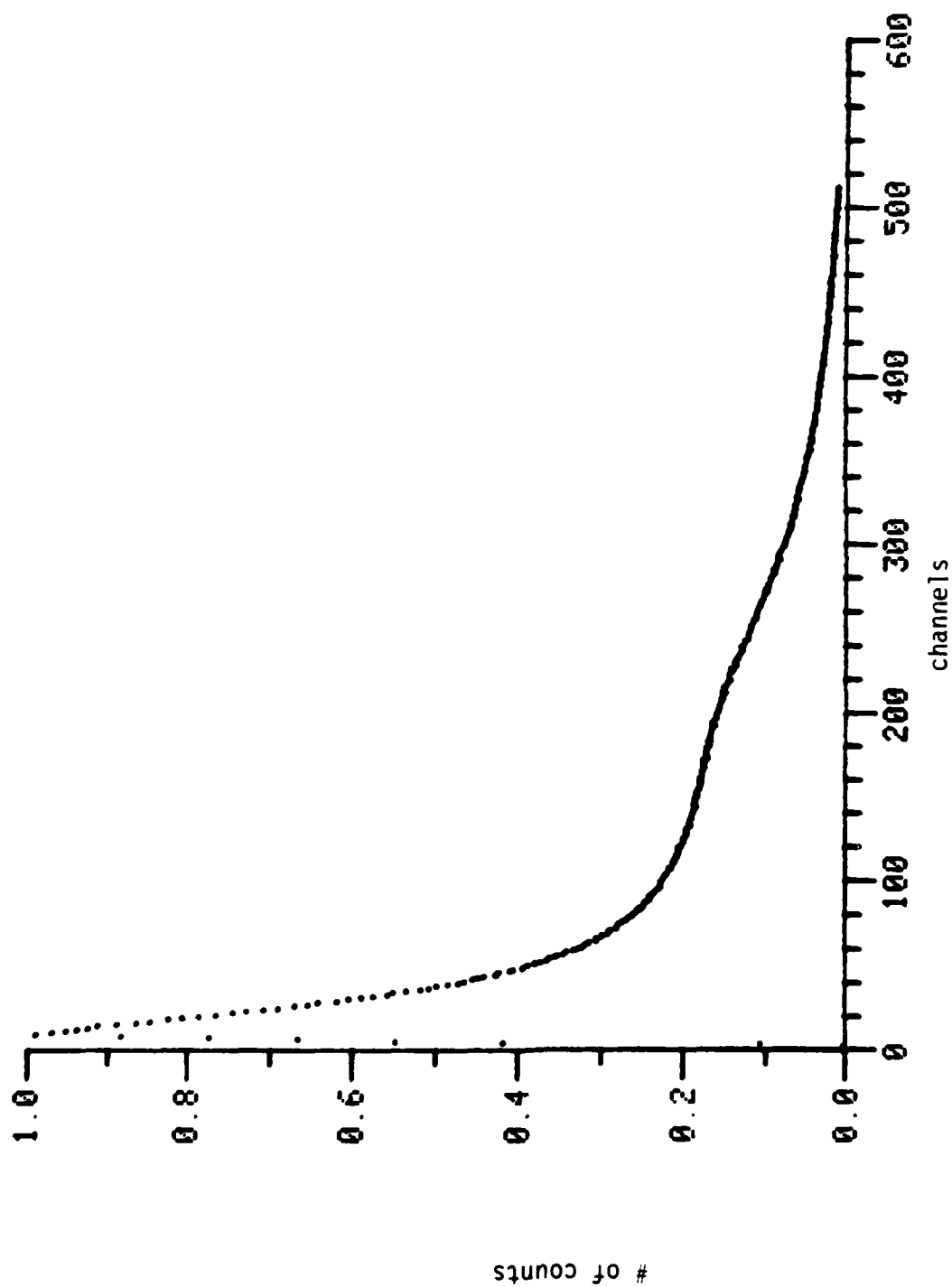


Figure 9.

$\times 10^5$ PULSE HEIGHT VS. GAS SETTING [400/MIN; 1100VDC]



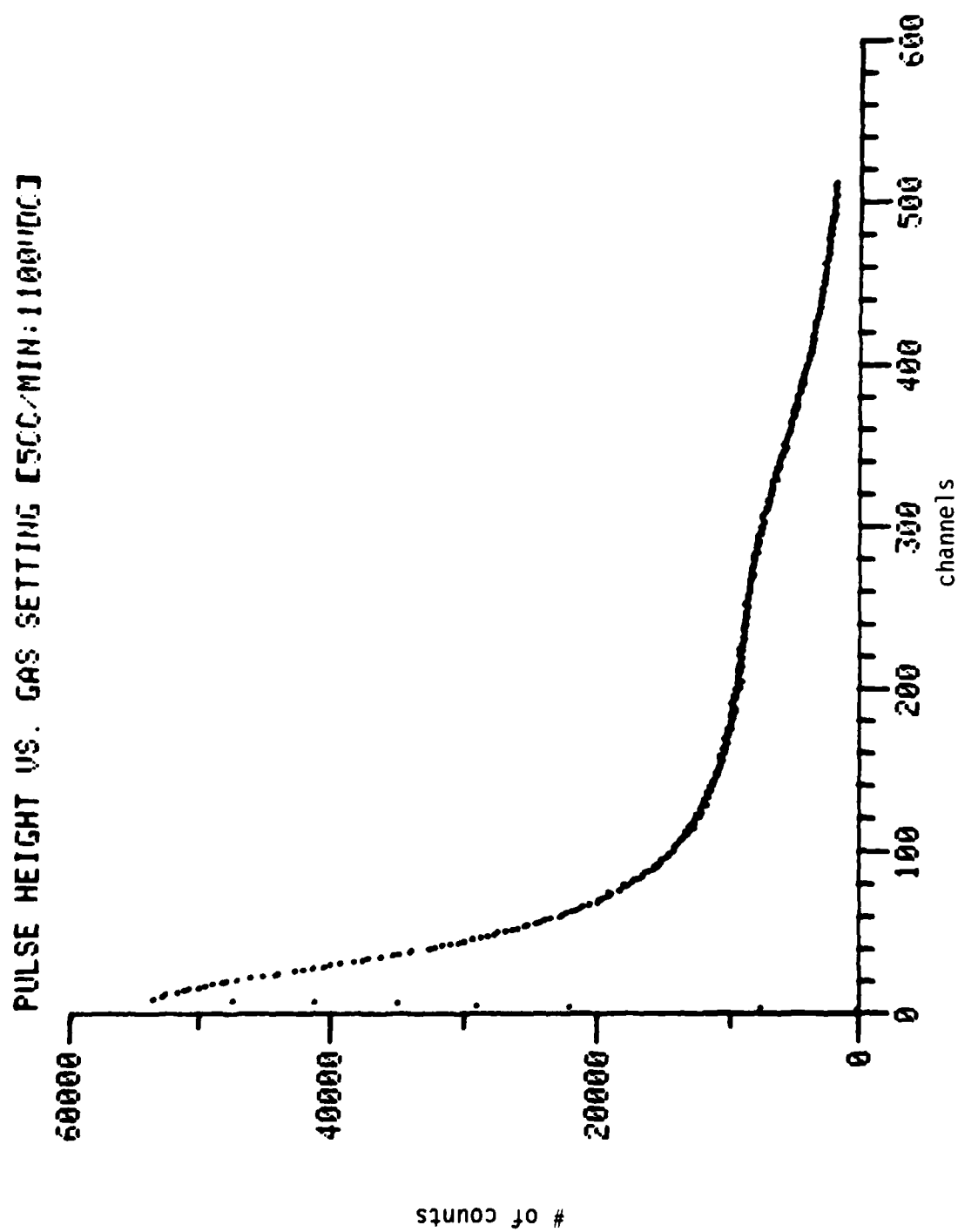
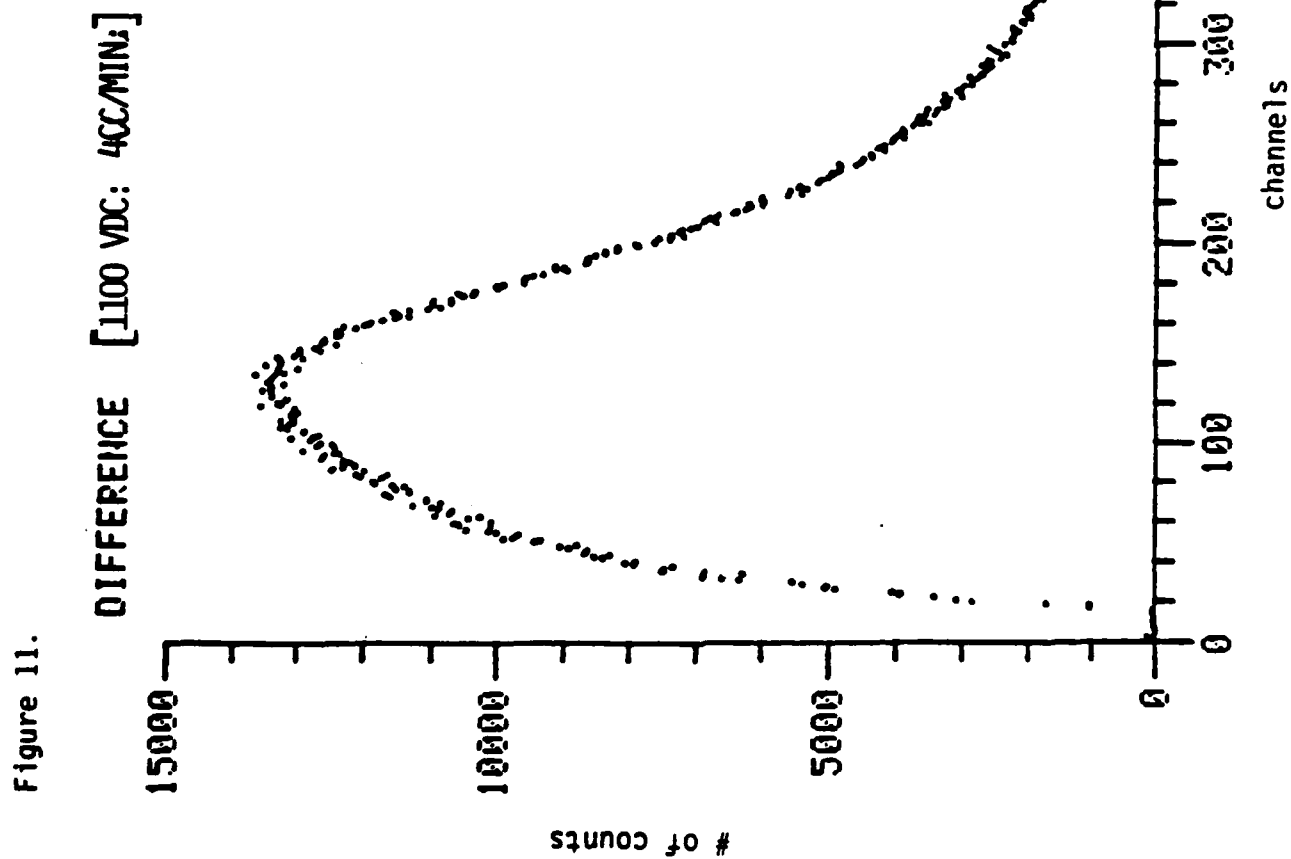


Figure 10.



III. CONVERSION ELECTRON MÖSSBAUER SPECTROSCOPIC (CEMS) RESULTS

In order to do conversion electron Mössbauer spectroscopy one must set an energy window at the appropriate location on the pulse height electron energy distribution curve. One attempts to select the energy region that will give the best signal-to-noise ratio in the resulting spectrum. Once this energy window has been selected the pulses which lie therein are fed to the input of the multichannel analyzer. The multichannel analyzer is now operated in the multichannel scalar mode. In this mode, the multichannel analyzer is swept through all its channels in synchronization with the velocity of the source drive. Thus each channel on the multichannel analyzer now corresponds to a particular source velocity. At those velocities, which result in doppler-shifted gamma rays having the correct energy to be resonantly absorbed by the sample ^{57}Fe nuclei, conversion electrons are produced. Thus CEMS spectra show peaks at these resonant energies, in addition to a non-resonant flat background.

Fig. 12 shows a CEMS result for a sample of 30% enriched ^{57}Fe in a 6 μ thick rhodium foil. If one defines the signal-to-noise ratio (S/N) as the height of the resonant peak minus the background level divided by the background, the S/N result shown is ~ 20 to 1. Fig. 13 shows a similar result using a sample of unenriched 0.001" thick stainless steel foil. The natural abundance of ^{57}Fe in iron is about 2%. Notice that, as expected, the S/N is less than for the enriched sample. The S/N for the unenriched stainless steel foil is about 3 to 10.

It is common in iron Mössbauer spectroscopy for iron foils to be used for calibration purposes. This is done because the positions of the six peaks in such spectra are known very accurately. Such results are used to calibrate spectra when the drive electronics is set on a particular velocity

Figure 12.

CEMS SPECTRUM OF ENRICHED 30% FE/RH FOIL 3 APRIL, 1984

velocity setting = $\pm 2.00\text{ms}^{-1}$

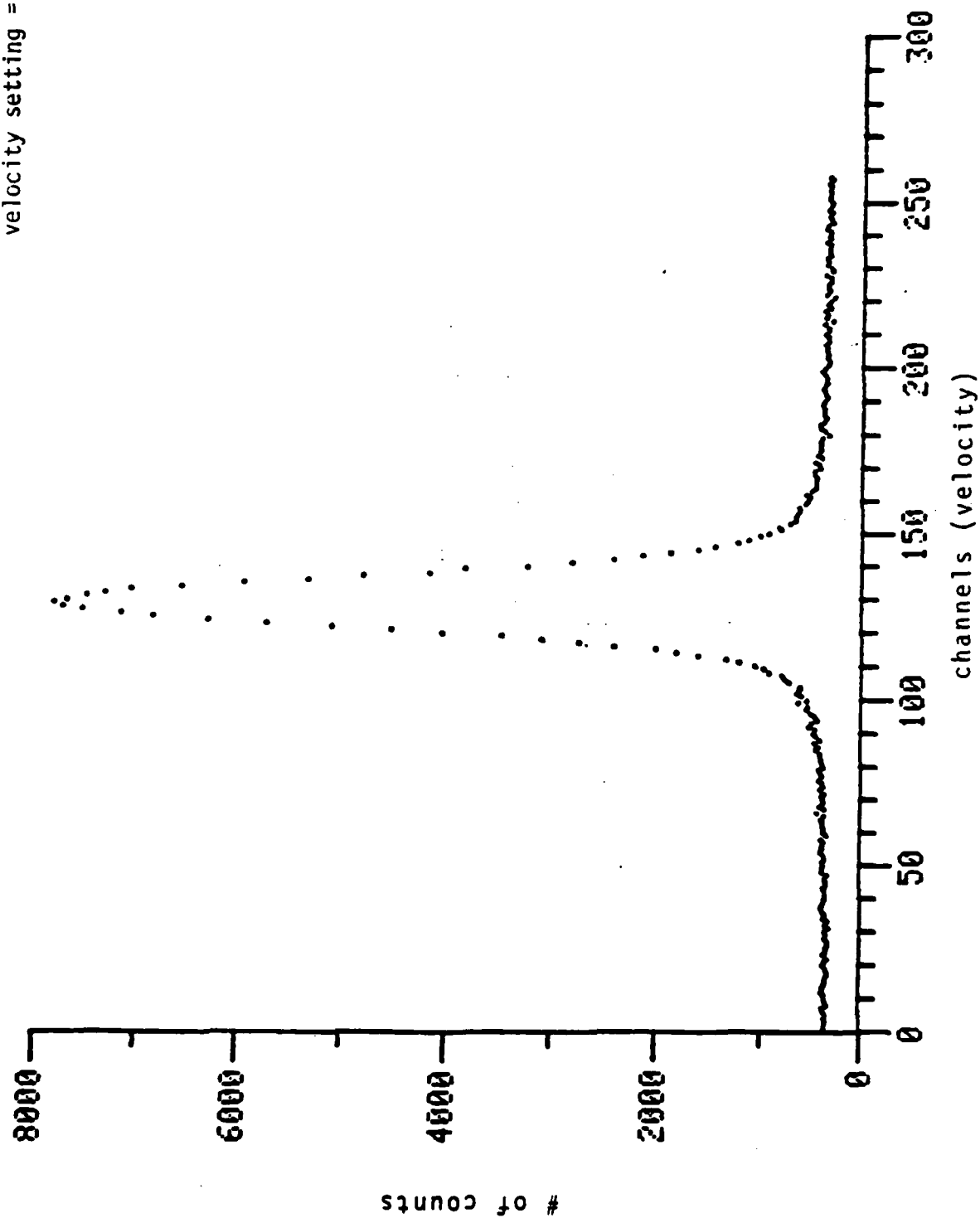
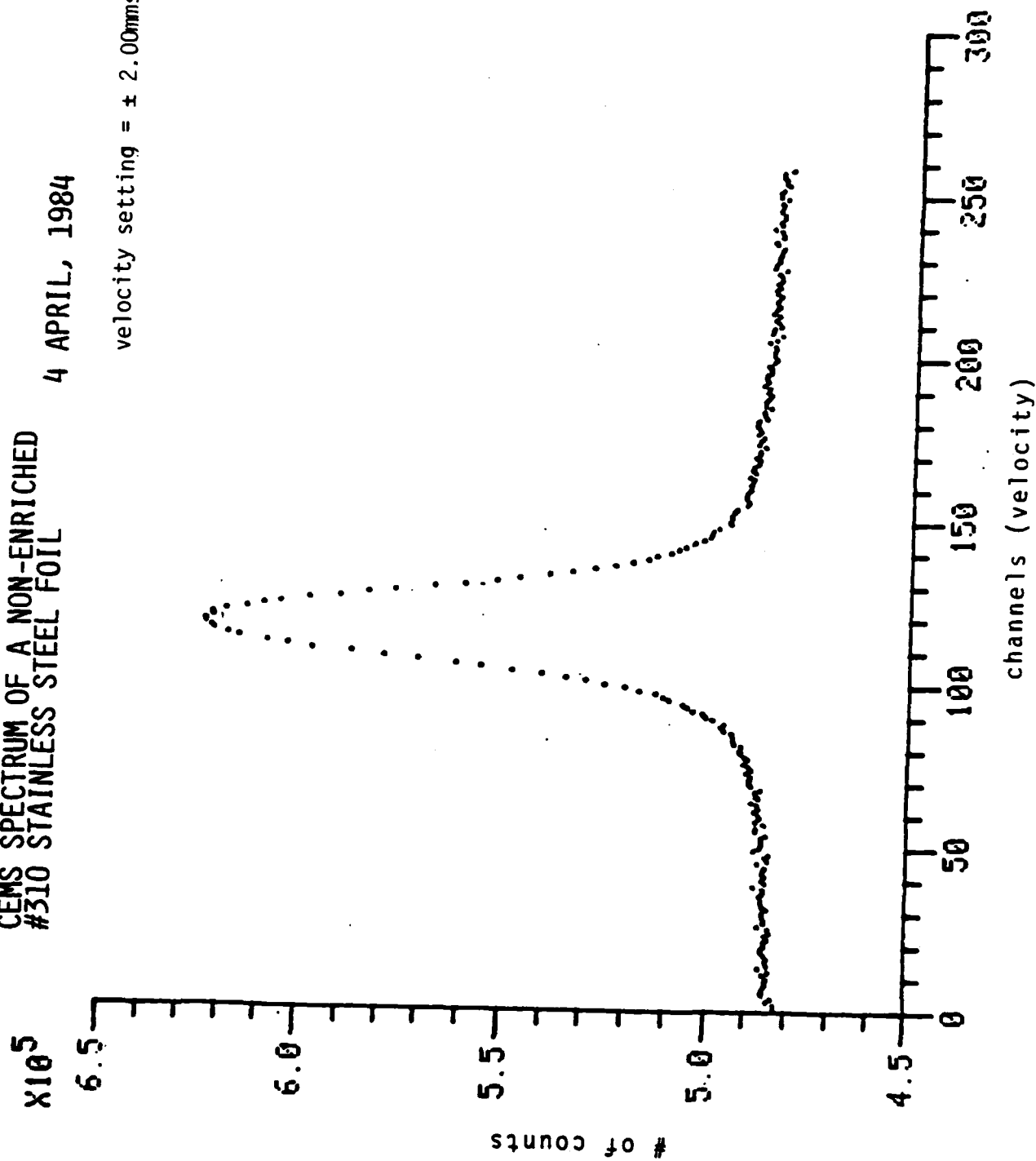


Figure 13.

CEMS SPECTRUM OF A NON-ENRICHED
#310 STAINLESS STEEL FOIL

4 APRIL, 1984

velocity setting = $\pm 2.00\text{mms}^{-1}$



setting. In Figs. 14, 15, and 16, the spectra of a 2 μ thick, 95% enriched iron foil are presented for three different maximum velocity settings. In Fig. 14 we see all six peaks of the spectrum. In Fig. 15, results are presented when the velocity scale is expanded so that only the four inner peaks of the iron foil spectrum are visible. Finally, the velocity scale is expanded still further, and results showing just the inner two peaks of the iron foil sample spectrum are shown in Fig. 16.

IV. RESULTS ON InP: ^{57}Fe SAMPLES

The Naval Research Laboratory (Dr. P. E. Thompson and Dr. R.L. Henry) has supplied InP: ^{57}Fe samples. These samples were prepared by the Czochralski method in which the InP was doped with ^{57}Fe and pulled from the melt. As a consequence of the limited solubility of iron in InP, the resulting boule consisted of regions of substitutional iron near the top of the boule, while lower portions contained iron precipitates. Because of the low concentration of substitutional iron, we have, so far, only obtained CEMS results for the precipitate iron region.

Before attempting a CEMS measurement on the samples provided by the Naval Research Laboratory, it is important to determine the background or "noise" pulse height spectrum of electrons for this case. This is needed in order to select the best energy window, thus optimizing the S/N. Fig. 17 shows the electron energy distribution pulse height spectrum for both the "on" resonance result for the enriched iron in rhodium sample and the "off" resonance result for the InP:Fe (sample #71) sample. It is clear that the background shape, i.e. the "noise" spectrum, is different for the two cases.

The 7.3keV conversion electron shoulder falls at about channel 200 for these settings. From the results shown in Fig. 17 it is reasonable to set

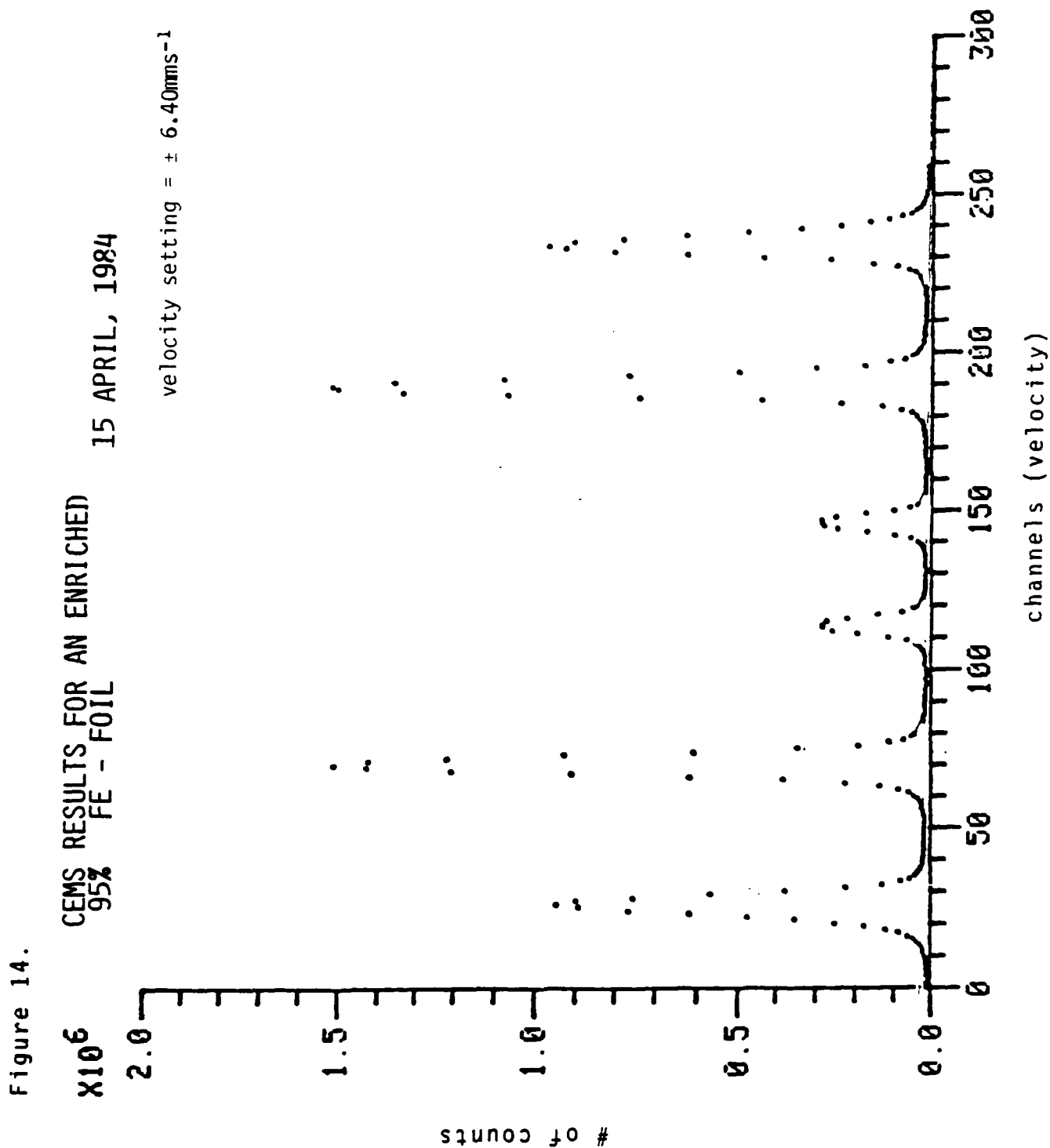
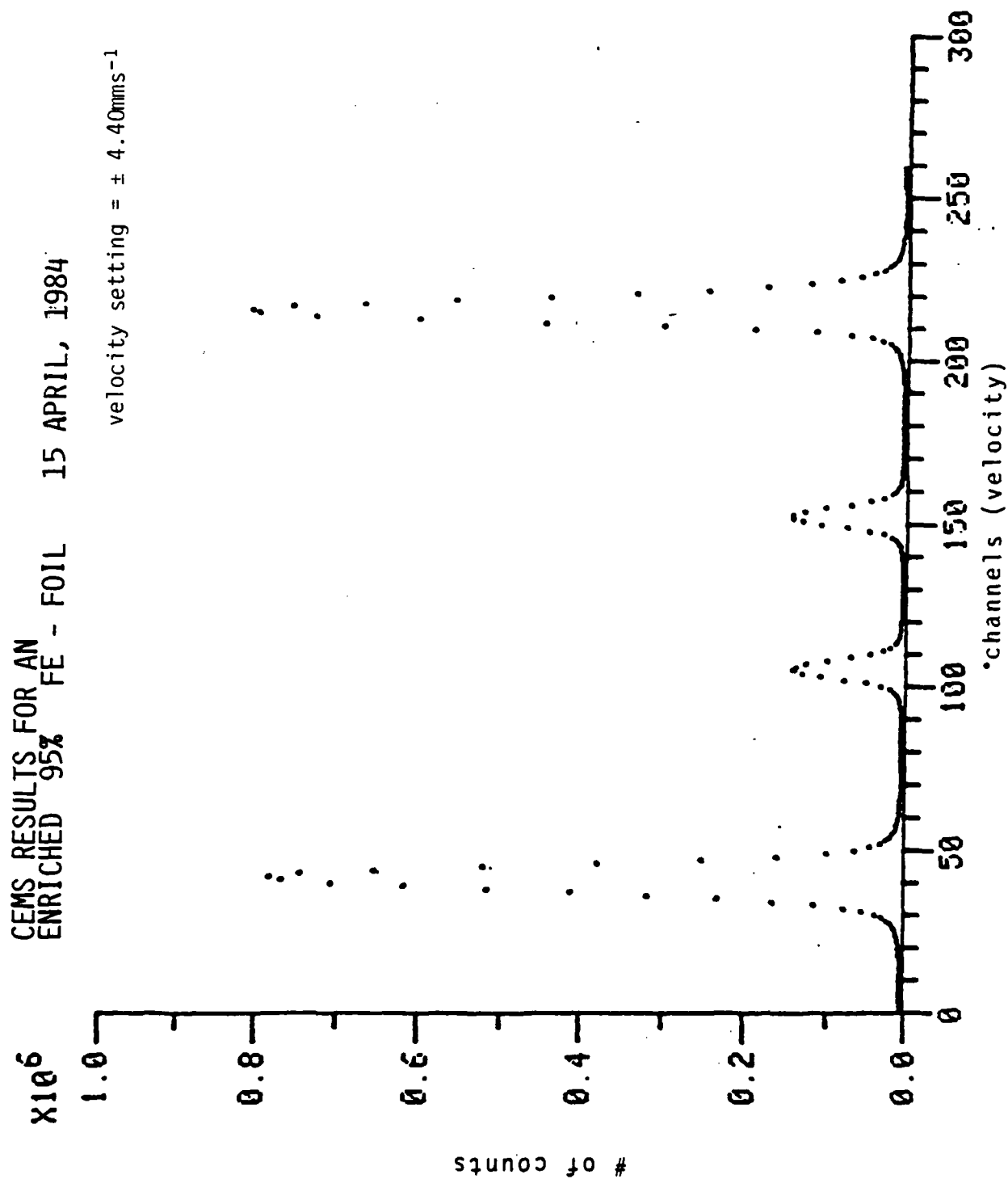


Figure 15.



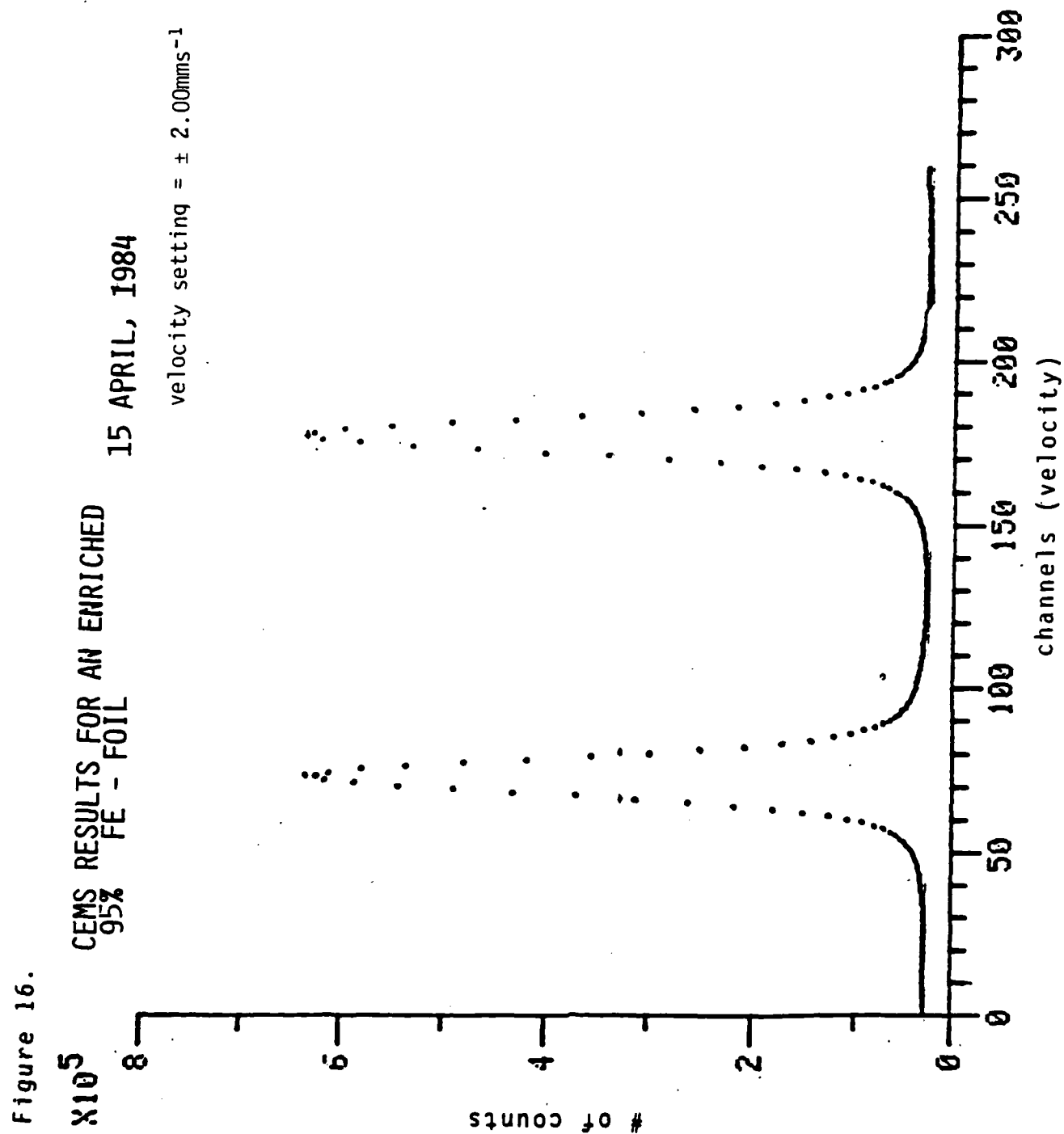
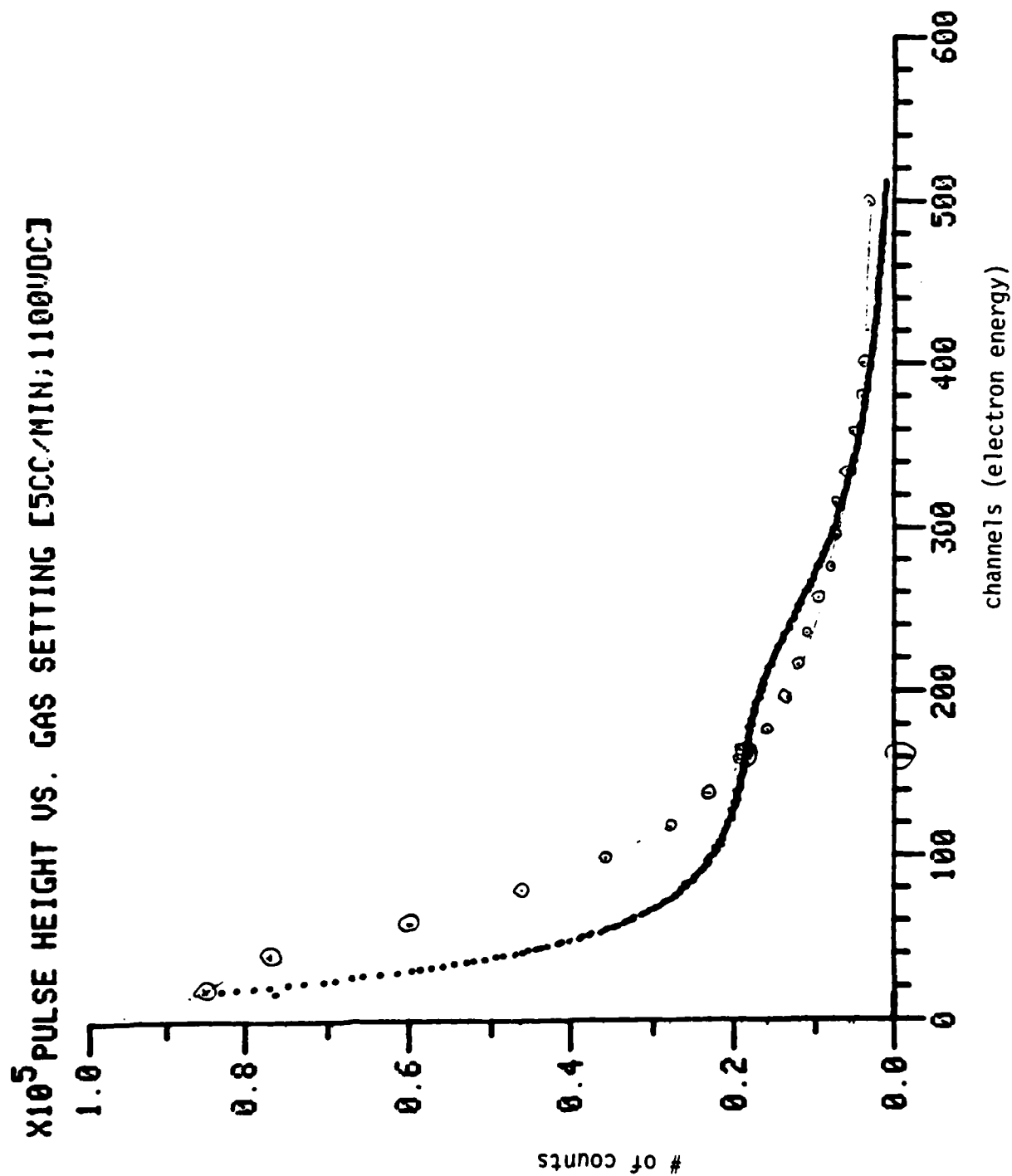
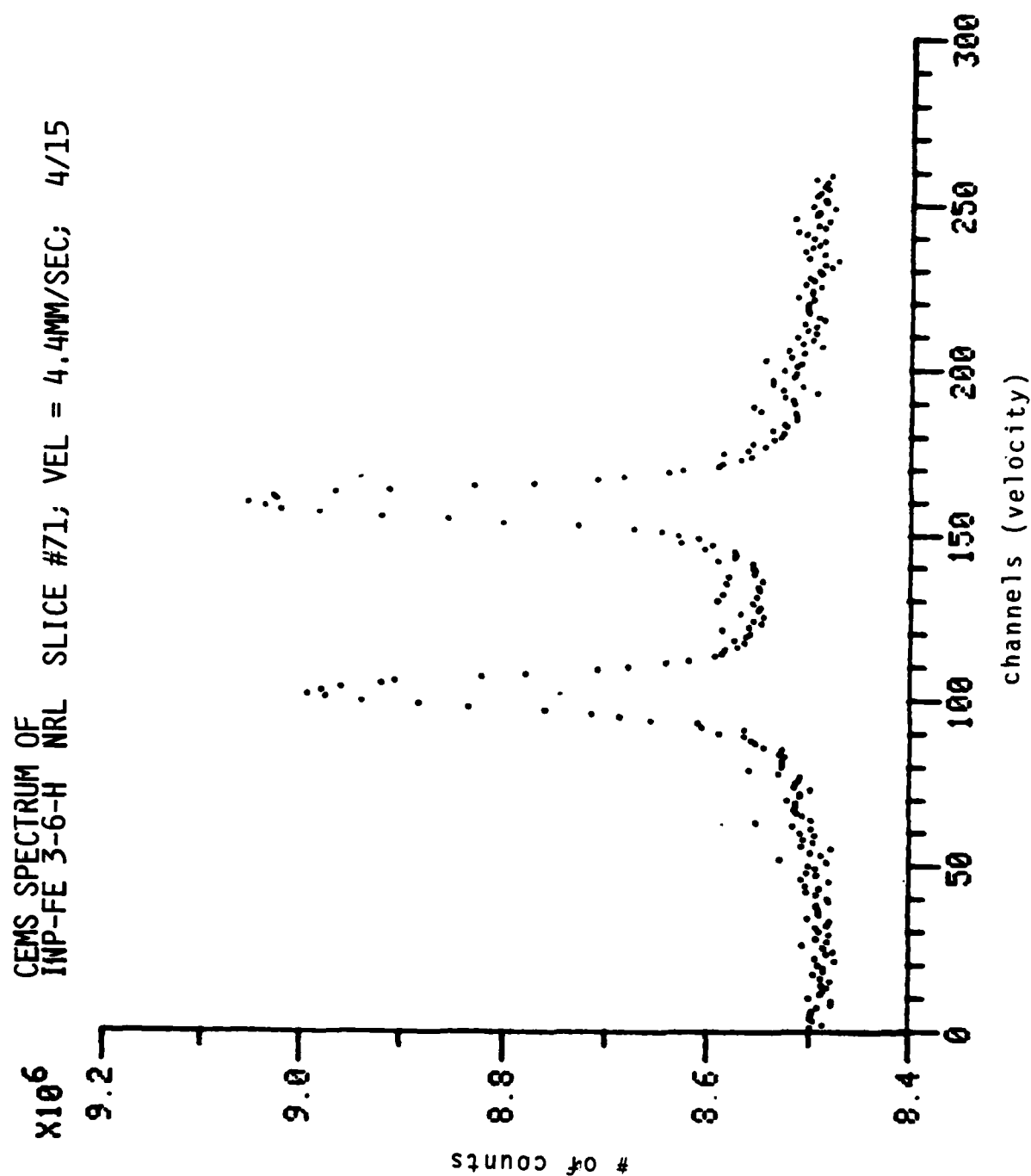


Figure 17.



the lower level of the energy window at a value somewhat above channel 160. Setting the energy window lower level at this point and opening the window upper level wide open, results in the CEMS spectrum for sample #71 as shown in Fig. 18. This spectrum clearly shows the iron phosphide precipitate. Based on previous Mössbauer effect results,⁴ we tentatively identify the precipitate as FeP_2 . However, the x-ray analysis done at the Naval Research Laboratory⁵ on slice #72, adjacent to #71, indicated that the atomic percentage was approximately the same for iron and phosphorous. This shows that there is an equal number of atoms of iron and phosphorous. This would suggest that the precipitate might be FeP . Our results would not support this hypothesis. Further consideration of Fig. 18 shows that the scatter of data in the flat background is greater than one would expect from statistics. This may indicate that the precipitate region consists of both FeP_2 and pure iron components. We plan to continue our study of the nature of the precipitates and then quickly move on to a careful study of the samples that show iron as a substitutional component only. Our aim is to study the substitutional iron in samples having no precipitates. Whether we can detect the low concentration of iron in such samples should be determined in the next three months.

Figure 18.



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